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CHEMICAL AND ELECTROCHEMICAL STUDIES IN ROOM TEMPERATURE

ALUMINUM HALIDE-CONTAINING MELTS

by

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This review of recent work in the area covers a brief overview of work in sodium tetrachloroaluminate melts, with emphasis on acid-base chemistry, species characterization, chemistry of chalcogenides and chalcogens and the stability of radical ions. Work in the aluminum chloride-n-butylpyridinium room temperature melt is covered in more detail with regard to species characterization by Raman spectroscopy, acid-base chemistry, the electrochemical and spectroscopic studies of aromatic hydrocarbons, and an indication of other studies of inorganic species in these melts.

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1. INTRODUCTION

Molten salts have been used in industrial processes, such as for the production of aluminum, for many years. Applications in areas of molten salt battery systems, molten salt nuclear reactors, extraction from metal ores, electrorefining, etc., have prompted researchers to study the fundamental properties of molten salt systems for the past 30 years.[1] Recently, due partly to the relatively low working temperatures (150-200°C), the molten aluminum halides have been widely studied, e.g., AlX_3/MX, where M^+ is an alkali metal cation.[1] Very recently, work on "room temperature" AlX_3 based systems has been initiated.

The primary scope of this review is the room temperature molten salt systems based on aluminum halides; however, it is pertinent to review some of the properties of the higher temperature aluminum halide-alkali metal halide melts as background for the discussion of the low temperature systems.

Several aspects of the chemistry of chloroaluminate melts have been reviewed. Boston[2] reviewed the molten salt chemistry of haloaluminates up to 1971 covering physical properties, solvent properties, some aspects of electrochemical and spectroscopic studies. Fung and Mamantov[3] detailed the electroanalytical chemistry of molten salts, particularly of molten haloaluminates, emphasizing the electrochemical behavior of the inorganic solutes that had been studied with emphasis on transition metal ions. Jones and Osteryoung[4], in 1975, reviewed organic reactions in molten tetrachloroaluminate solvents of the type: condensation-addition, dehydrogenation-addition (Scholl reactions) and rearrangement-isomerizations. Plambeck[5] summar-

ized the various inorganic systems studied in these melts, hydrogen, elements of the groups IIIA, IVA, VA, VIA, VIIA, as well as transition metal elements, including actinides. A summary of electromotive force series in the 50:50 mole percent $AlCl_3$:NaCl at 175°C is presented. Mamantov and Osteryoung[1] described the acid-base dependent redox chemistry in molten chloroaluminates, basically from the point of view of the authors' own research.

With this brief introductuion it is now appropriate to consider aspects of the chemistry which makes the chloroaluminate systems unique.

2. ALUMINUM HALIDE-ALKALI METAL HALIDE MOLTEN SALT SYSTEMS

    2a. Acid-Base Chemistry

    The aluminum halide-alkali metal halide melts display wide acidity
changes with varying melt compositions. The acid-base properties can deter-
mine the redox and coordination chemistry in these media and several research
groups have investigated this particular aspect over the past ten years.[6-10]
The acid-base chemistry of the $AlCl_3$/NaCl molten salt system, in the range
49-70 mole percent of $AlCl_3$, can be represented[9,10] by the following three
equilibria (175°C):

$$2 \ AlCl_3(\ell) \ \overset{\rightarrow}{\leftarrow} \ Al_2Cl_6 \ (\ell) \qquad (K_0 = 2.86 \times 10^7) \tag{1}$$

$$AlCl_4^- + AlCl_3 \ \overset{\rightarrow}{\leftarrow} \ Al_2Cl_7^- \qquad (K_2 = 2.4 \times 10^4) \tag{2}$$

$$2 \ AlCl_4^- \ \overset{\rightarrow}{\leftarrow} \ Al_2Cl_7^- + Cl^- \qquad (K_m = 1.06 \times 10^{-7}) \tag{3}$$
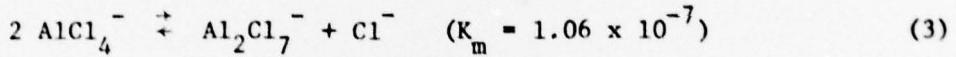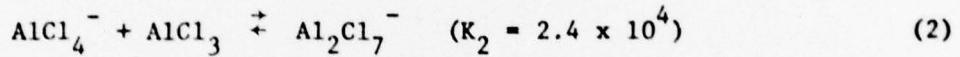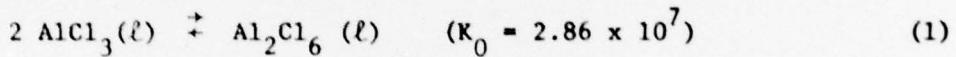
where the K values are on the mole fraction scale. The dominant acid-base
equilibrium is described by Eq. 3 where $Al_2Cl_7^-$ is the Lewis acid and the Cl^-
is the base. This equilibrium is an autosolvolysis reaction, analogous to
water autoprotolysis. The pCl^- ($-log[Cl^-]$), on the mole fraction scale, of a
neutral melt (1:1 $AlCl_3$:NaCl) is 3.5 at 175°C. At this composition, the
system can be considered essentially as $Na^+AlCl_4^-$. This melt can be made
more acid (excess $AlCl_3$) by anodizing an Al wire[10] or by addition of $AlCl_3$.
The melt can be made more basic (excess NaCl) by cathodizing an Al wire or
by addition of NaCl. An Al electrode is employed to monitor the melt's
acidity.[9] At 175°C, the pCl of the most basic melt saturated in NaCl is
1.1. The major acidity (pCl) changes occur in the vicinity of the 1:1
$AlCl_3$:NaCl mole ratio.

2b. Species Characterization.

The nature of the species present in these equilibria has been studied by Raman spectroscopy.[11-15] Mamantov et al.[11] have reported Raman spectra of sodium chloroaluminate melts and have reported evidence for species $AlCl_4^-$, $Al_2Cl_7^-$, Al_2Cl_6, and possibly $Al_3Cl_{10}^-$.[11] For the $AlCl_4^-$ species, the major Raman vibrational frequencies and their respective polarizations were: 351 (P); 121 (D); 490 (D); and 186 (D) cm^{-1}, in order of decreasing intensity. For pure molten Al_2Cl_6, the major Raman-active frequencies were 341 (P); 218 (P); 119 (D); 104 (P) cm^{-1}. By assuming that in the 50/50 to 58/42 mole percent $AlCl_3$/NaCl range, the only Raman-active species are $AlCl_4^-$ and $Al_2Cl_7^-$, the following vibrational frequencies were assigned to $Al_2Cl_7^-$: 313 (P); 432 (P); ~100 (D); and ~165 (D) cm^{-1}. Due to overlap of broad bands of $AlCl_4^-$ at 121 and 186 cm^{-1}, the frequencies at 100 and 165 cm^{-1} were only estimated. Since the spectra in the high acidity range (>66 mole percent $AlCl_3$) displayed other bands which could not be explained solely on the basis of $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6, species such as $Al_3Cl_{10}^-$ were postulated.[11] Raman spectra of the corresponding bromide and iodide melts have also been reported.[13]

Raman spectroscopic data for the potassium chloroaluminate melts have been reported by Oeye and coworkers.[12,14] Spectral data for $AlCl_4^-$ agree well with those found in the sodium chloroaluminate melt.[11] The four absorption bands of $AlCl_4^-$ verify T_d symmetry. Better low frequency spectroscopic data for $Al_2Cl_7^-$ were also obtained[12,14]: 99 (D); 164 (D); 312 (P); and 435 (D) cm^{-1}. An earlier report[15] of Raman spectra of the 50/50 mole percent $AlCl_3$/KCl indicated a much larger number of bands (9) than observed for $AlCl_3$/NaCl (4). This melt was related to a distorted $AlCl_4^-$ (C_{2v}).[15]

According to Maroni and Cairns,[16] a number of the reported bands are weak and poorly defined and may be spectral artifacts.

A normal coordinate analysis for $Al_2Cl_7^-$ assuming a D_{3d} model with a linear Al-Cl-Al bridge does not reproduce the experimental frequencies.[12] Structural determinations[17] by X-ray crystallography on the analogous $Al_2Br_7^-$ ion either as a potassium or ammonium salt show that the anion consists of two $AlBr_4^-$ tetrahedra sharing one corner in a staggered arrangement with a bent Al-Br-Al bridge (109.3^O and 107.7^O respectively for the K^+ and NH_4^+ salts). The symmetry of the $Al_2Br_7^-$ anion is close to C_{2v}. Structural determinations by the NQR double-resonance technique confirmed the structure of $Al_2Br_7^-$ and led to a reasonable qualitative bond model for this ion.[18] The structure of the compound $Te_4(Al_2Cl_7)_2$[19] was determined and the $Al_2Cl_7^-$ anion also consists of two tetrahedra sharing one corner in staggered arrangement with a bent Al-Cl-Al bridge (110.8^O). Normal coordinate calculations assuming similar symmetry for the $Al_2Cl_7^-$ anion might yield better agreement between calculated and experimental frequencies, but is clearly more difficult to do.

2c. Electrochemistry of the Chalcogenide Ions and Chalcogens

Mamantov et al.,[20,21] and Paulsen and Osteryoung[22] have studied the electrochemistry of sulfur and sulfide. Sulfur has been quanitatively reduced in both acid and basic melts at 175^OC. Nernst plots for the sulfur/ sulfide redox couple have a slope corresponding to a four-electron process, described as

$$S_2 + 4e^- \rightleftharpoons 2S^{2-}.$$
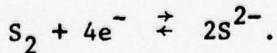
The electrochemistry of oxide and chalcogenide ions in these molten salt systems was more quantitatively investigated by Osteryoung and coworkers[23-26].

By titrating O^{2-}, S^{2-}, Se^{2-}, or Te^{2-} species in the melt with electrogenerated $Al_2Cl_7^-$ ions, it was shown that in the basic to neutral melts these ions behave as dibases as described by the equilibrium:

$$X^{2-} + 2 \, Al_2Cl_7^- \; \overset{\rightarrow}{\leftarrow} \; AlXCl_2^- + 3 \, AlCl_4^- \qquad (4)$$
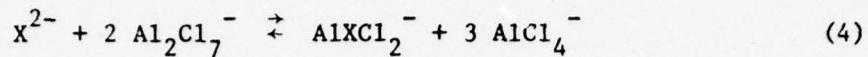
where $X^=$ may be $O^=$, $S^=$, $Se^=$, or $Te^=$, whereas in neutral to acidic melts they became tribases, the equilibrium then becoming:

$$X^{2-} + 3 \, Al_2Cl_7^- \; \overset{\rightarrow}{\leftarrow} \; AlXCl + 5 \, AlCl_4^- \qquad (5)$$
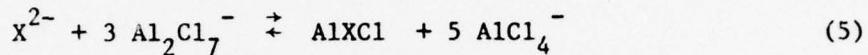
The base strength of the ions in the acid melt was found to be in the order $O^{2-} > S^{2-} > Se^{2-} \simeq Te^{2-}$. [24]

Oxide does not appear to be electroactive[23] in this molten salt system (cf. ref. 1) but the electrochemistry of sulfur[22], selenium[26], tellurium[25], and their compounds has been thoroughly investigated using a variety of electrochemical methods. Sulfur was shown to oxidize very close to the anodic limit of the melt and it is therefore uncertain what the nature of the oxidation product is though in basic melts it appears to be S_2^{2+} whereas in acidic melts some higher oxidation state species appears likely. Spectrophotometric, potentiometric, and Raman data[27] indicate that the oxidation product is a S(IV) species. Addition of $SCl_3^+AlCl_4^-$ [28] to the melts reproduces the electrochemical and spectral behavior[1,27] observed in the electrochemical oxidation of sulfur.

The electrochemical behavior of selenium[26] is similar; it is reduced to selenide, more reversibly than sulfur is to sulfide, and can be oxidized to Se(IV). In basic melts this oxidation goes via a stable Se(II) intermediate whereas in acidic melts the oxidation is directly to Se(IV). The behavior of tellurium[25] is rather different as the metal is insoluble in the melt. In the most basic melts at temperatures above 250°C, Te(IV) is initially reduced

to a soluble Te(II) species, and then to the metal. In more acidic melts and at lower temperatures the Te(IV) is reduced directly to Te. Te metal rapidly reacts with Te(IV) to form Te_4^{2+}.

The nature of the chalcogen species involved in chloroaluminate melts, as determined by an interesting combination of potentiometric and spectro-phometric studies by Bjerrum and coworkers has been reviewed recently[27]. For instance, entities such as Te_2^{2+}, Te_4^{2+}, Te_6^{2+}, and Te_8^{2+}, stabilized by the large anions, $AlCl_4^-$ and $Al_2Cl_7^-$, are present in the melt as well as Te^{2+}, which is stabilized by Cl^-.[27,29,30] Bjerrum and coworkers[31,32] have also studied the chloro-complexes of the Te^{4+} cation in $AlCl_3/KCl$ melts and found the complexes $TeCl_6^{2-}$, $TeCl_5^{2-}$, $TeCl_4$, and $TeCl_3^+$, which are linked by melt acidity dependent equilibria. $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$, where formally the tellurium is in a ½ oxidation state, have been isolated and character-ized.[18,33] This agrees with earlier data by Bjerrum and Smith.[34]

Similarly, Bjerrum and coworkers[27] have presented evidence for ions: Se_4^{2+}, Se_8^{2+}, Se_2^{2+}, Se_{16}^{2+} as the most likely other low oxidation states formed by reduction of Se(IV) with elemental selenium. The Se(IV) species is $SeCl_3^+$ in most of the basic and most of the acidic range as deduced from spectro-scopic and potentiometric data. For sulfur[35] the most consistent interpre-tation of potentiometric and spectrophotometric data was S_2^{2+}, S_4^{2+}, S_8^{2+}, S_{16}^{2+}, together with S(II) and S(IV) most likely as SCl_3^+.

2d. Stability of Radical Ions

From a chemical point of view, another interesting finding is the stability of radical ions in these melts. Several aromatic amine radical cations were shown to be remarkably stable in these melts[36] at 175°C, in comparison to the poor stability found in aprotic organic solvents.[4] It has been suggested that this stability is a result of the "totally" andydrous

nature of these melts, whereas most organic solvents contain varying

residual amounts of water depending on the purification procedure. Tri-

phenylamine,[36] N,N-dimethylaniline,[36,37] N,N,N',N'-tetramethylbenzidine,[38]

quinone-hydroquinone systems,[38] sulfur heterocycles,[40] were studied and

showed the interesting interplay of acid-base chemistry and redox processes

with radical cation stabilization.

3.   ROOM TEMPERATURE MOLTEN SALT SYSTEMS - INTRODUCTORY REMARKS

All the electrochemical and chemical reactions mentioned so far involve
temperatures greater than 150°C. It is very clear 1) that the operating
temperatures were above the boiling point of many organic solutes whose
electrochemistry could be of interest and 2) that rapid homogeneous reactions
could take place between melts and organic compounds.[4,41] For most other
applications of the haloaluminates, a melt system with similar solvent
properties operating at lower temperatures, e.g., room temperature, would
be advantageous.

In 1951 a melt composed of 67 mole percent aluminum chloride and 33
mole percent of the quaternary organic salt ethylpyridinium bromide (a 2:1
molar ratio), which is molten at room temperature, was reported by Hurley
and Wier.[42] Osteryoung and coworkers utilized this solvent for electro-
chemical and photochemical investigations.[43-46] The electrochemical
oxidation of iron diimine complexes was shown to be a reversible process.
Upon irradiation with low energy photons, the iron(II) diimine complexes
were shown to be converted to the corresponding stable iron (III) compounds,
with electron transfer to the acceptor ethylpyridinium cations.[46]

An interesting feature of the 2:1 $AlCl_3$:ethylpyridinium bromide melt
is its miscibility with co-solvents, e.g., benzene[42], toluene, etc. Hurley
and Wier[42] had observed that this mixed solvent system was better than the
pure melt for electroplating of aluminum. Upon dilution with benzene, the
conductivity of the solutions increases compared to the pure melt, while
the viscosity decreases. This solvent system, melt plus benzene, proved
very suitable to the study of organic[43,49] and organometallic[45] compounds.
An advantage of the mixed solvent is that a number of organic and organo-
metallic compounds, insoluble in the pure melt, are soluble in the melt
plus benzene.[45] In the 50%(v/v) melt and benzene solution hexamethyl-

benzene (HMB) can be anodically oxidized to pentamethylbenzene and diphenyl-
methane.[44] This was the first reasonable synthesis in a molten salt system,
where HMB can be selectively and quantitatively demethylated to mesitylene and
diphenylmethane in a Friedel-Crafts type reaction.[44] The same solvent system
has been employed to study the electrochemical oxidation of six metal carbonyls.[45]
Chromium hexacarbonyl and iron pentacarbonyl were found to be reversibly
oxidized to the corresponding seventeen electron cations.[45] In aceto-
nitrile, only the former compound was found to undergo reversible one-
electron oxidation.[48] However, this melt is not very suitable for investi-
gating acid-base dependent reactions, since decreasing the acidity by in-
creasing the ethylpyridinium bromide content raises the melting point sharply
at the 50:50 mole percent composition.

Similar systems based on toluene plus $AlBr_3$ and KBr in a 2:1 mole
ratio have been employed by Gileadi and coworkers[49-53] primarily with
interest in electroplating of aluminum.

4. ALUMINUM CHLORIDE - N-(n-butylpyridinium) CHLORIDE (BuPyCl) MOLTEN
   SALT SYSTEMS

Recently, the $AlCl_3$-N-(n-butylpyridinium) chloride system (1:1 mole
ratio) was found to melt at 27^oC, and the 2:1 mole ratio exists as a liquid
at temperatures well below ambient. In fact, a mole ratio range of 0.75:1
to 2:1 can be employed at temperatures only slightly greater than 27^oC, very
close to room temperature.[47,54]

4a. Species Characterization[54]

Raman spectroscopy has been used to study the species composition
of the molten salt system $AlCl_3$:BuPyCl over the 0.75:1 to 2.1:1 mole ratio
range[54] at 30^oC. Table I summarizes the experimental frequency shifts (cm^{-1})
for the vibrational peaks. To characterize these spectra, the peak positions
were compared to the assignments for $AlCl_4^-$ and $Al_2Cl_7^-$ (see above) in the
$AlCl_3$/MCl (M = Na^+, K^+) [11,12,14] melts, and the spectra of Al_2Cl_6 [11] (see
above) and n-butylpyridinium cation (major frequencies in order of decreasing
intensity in cm^{-1}: 1024; 125; 88-103; 644; 774). There is a straightforward
correlation between the frequencies: 351 (P); 126 (D); 484 (D); and 184 (D)
found in the low $AlCl_3$-content melts (0.75:1 - 1.0:1.0) and the frequencies
assigned to $AlCl_4^-$ anion[11,12,14]. As the $AlCl_3$-content increases, new
vibrational peaks at 102 (shoulder) (D), 163 (D), 315 (P), and 434 (P)
become dominant, and the bands assigned to $AlCl_4^-$ do not contribute to
the observed spectra within the experimental error. These frequencies
compare very well with the previously assigned frequencies for the $Al_2Cl_7^-$
anion, observed by Mamantov et al.[11] and Oeye et al.[12,14] (vide supra).
Due to the overlap of the strong peak at 315 cm^{-1} in the high aluminum
chloride content region or the strong peak at 351 cm^{-1} in the basic side,
and the major Al_2Cl_6 Raman active frequency at 341 cm^{-1}, Al_2Cl_6 cannot be

detected if present in small concentrations.

The molten salt system $AlCl_3$:BuPyCl can be described as follows as a function of composition.

<u>2:1 mole ratio of $AlCl_3$:BuPyCl</u> - At this mole ratio, the molten salt is best described as n-butylpyridinium dialuminum heptachloride, $BuPy^+Al_2Cl_7^-$. There is no evidence from the Raman spectra for the presence of $AlCl_4^-$ anions, contrary to what was observed in the $AlCl_3$-alkali metal halides.[11,12,14] These facts suggest that at this composition the association:

$$2 \ AlCl_4^- \ + \ Al_2Cl_6 \ \rightleftarrows \ 2 \ Al_2Cl_7^- \tag{6}$$
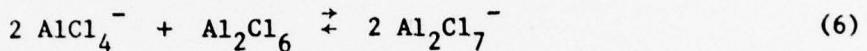
must be virtually complete.

<u>1:1 mole ratio of $AlCl_3$:BuPyCl</u> - The major aluminum containing component anion in this composition is the $AlCl_4^-$ anion. A small amount of the $Al_2Cl_7^-$ anion may be present at this composition (<u>cf</u>. band intensities at 433 cm^{-1}). Therefore, at this composition the melt contains $AlCl_4^-$, $Al_2Cl_7^-$, Cl^-, and possibly traces of Al_2Cl_6. Thus, the equilibrium:

$$2 \ AlCl_4^- \ \rightleftarrows \ Al_2Cl_7^- \ + \ Cl^- \tag{7}$$
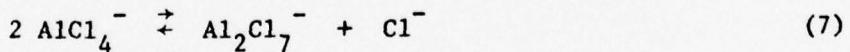
identical to the dominant equilibrium in the $AlCl_3$/NaCl systems, (Eq. 3), may be considered to exist in the room temperature molten salt.

At intermediate compositions it is possible to estimate the ratio of the mole fractions of $Al_2Cl_7^-$ and $AlCl_4^-$ species by assuming that these mole fractions are proportional to the integrated intensity of the strongest bands for each species.[54,12] The ratios of 1.2:1 and 3.3:1 were obtained

respectively for the 1.5:1.0 and 1.75:1.0 molar ratios of $AlCl_3$:BuPyCl. Therefore, as the melt becomes $AlCl_3$-rich, the molar excess of $AlCl_3$ is converted into $Al_2Cl_7^-$. At the limit, the 2:1 mole ratio $AlCl_3$:BuPyCl, this species is the major and possibly the only aluminum-containing species in the melt.

The large organic pyridinium cation does not influence the absorption frequencies of the anionic species, $AlCl_4^-$ or $Al_2Cl_7^-$. This finding agrees well with previous data by Rytter and Oeye[58] on the influence of the alkali metal cation size on the absorption frequencies of $AlCl_4^-$ anion. The smaller cation, Li^+, affects strongly asymmetric vibrations, whereas practically identical frequencies are obtained for Na^+ and K^+ within experimental error.

The major effect of the organic cation is to promote more extensive $Al_2Cl_7^-$ formation at the 2:1 mole ratio than is found in the higher temperature haloaluminate-alkali metal halide molten salt systems.

4b. Acid-Base Chemistry[55]

In order to quantify[55] the equilibrium described by Eq. 7 in the basic region, potentiometric titrations were carried out, by using an aluminum reference electrode, which behaves as a reversible chloride activity indicator electrode. From the Nernst equation:

$$E = E_o + (RT/3F) \ln(a_{Al^{3+}}/a_{Al(O)}) \tag{8}$$

incorporating the association constants for reactions (7) and formation of $AlCl_4^-$:

$$Al^{3+} + 4 Cl^- \rightleftharpoons AlCl_4^- \tag{9}$$
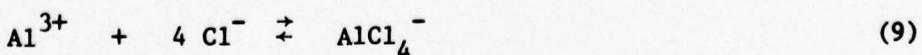
one obtains the following relation:

$$E = (RT/3F) \ln (a^o_{AlCl_4^-}/a^1_{AlCl_4^-}) + (4RT/3F) \ln (a^1_{Cl^-}/a^o_{Cl^-}) \qquad (10)$$

where superscripts o and l refer to reference and variable states, respectively.

The description of the electrochemical cell can be given as follows:

Al | BuPyCl, AlCl$_3$(ref) | fritted disc | AlCl$_3$(c), BuPyCl | Al
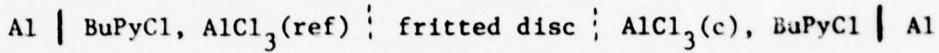
where BuPyCl = n-butylpyridinium chloride. Figure 1 shows some results of potentiometric titrations in the 2.0:1.0 to 0.6:1.0 molar ratio of AlCl$_3$:BuPyCl at 30, 60, and 120°C. The sigmoidal curves in Figure 1 differ considerably from those obtained for the AlCl$_3$/NaCl system.[9,10] First, the potential difference between the two plateau regions is 2-3 times larger than that observed in the high temperature melts indicating a greater pCl change in the low temperature melt. Second, a change in the slope of the curve in the acid region is observed in the low temperature but not in the AlCl$_3$/NaCl system.[9] Third, in the basic portion of the curve, potentiometric data are less reproducible than those in the acid region, due to the appearance of a blue colored species at the Al electrode, indicating that secondary reactions are taking place.

From the potentiometric data it is possible to assess an approximate conditional equilibrium constant for Eq. 7 by using Eq. 10

$$K = \frac{[Al_2Cl_7^-][Cl^-]}{[AlCl_4^-]^2} = 3.8 \times 10^{-13} \qquad (30°C)$$

The solid line in Figure 1 is a potential function represented by Eq. 10 with this equilibrium constant. The model is inappropriate in the acid region above 2:1 ratio.

In the basic region mixed potentials are measured due to the

spontaneous reduction of $BuPy^+$ cations by elemental aluminum. Therefore, the constant K, determined by calculations over the entire acid and basic range, is a lower limit because of the positive shift in the measured potential due to the $BuPy^+$ reduction.

A plot of the species distribution in this system from the 0.6:1.0 to the 1.8:1.0 mole ratio of $AlCl_3$:BuPyCl is shown in Figure 2. It is interesting to note that the chloride ion mole fraction almost spans the range found in the proton/hydroxyl equilibrium in water.

The potentiometric curves at higher temperatures up to 175^oC can also be characterized solely on the basis of Eq. 7. At 175^oC, $K < 1.19 \times 10^{-8}$, similar, but less than 1.06×10^{-7},[9] the constant for this equilibrium in the $AlCl_3$/NaCl system. These findings are consistent with the data of Torsi and Mamantov[59] for the $AlCl_3$/alkali metal halide systems which indicate that the greater the polarizing power of the cation, the larger the autosolvolysis constant at a given temperature.

When comparing spectroscopic and potentiometric data for the $AlCl_3$/alkali metal halide and $AlCl_3$/BuPyCl systems, one can observe that whereas in the former Al_2Cl_6 is a species present throughout the studied composition and temperature ranges, being particularly important on the acid side, this Lewis acid does not seem to be a component of the room temperature molten salt. Even at temperatures as high as 175^oC, little aluminum chloride vapor is detected over the 2:1 $AlCl_3$:BuPyCl melt. For the $AlCl_3$:BuPyCl system in the molar ratios of 0.75:1 to 2:1, the acid-base chemistry is described by Eq. 7, whereas for the $AlCl_3$/alkali metal halides two additional equilibria involving $AlCl_3$ and Al_2Cl_6 (Eqs. 1 and 2) must be invoked.

4c. Electrochemical and Spectroscopic Studies of Aromatic Hydrocarbons[56]

The electrochemical oxidation of twelve aromatic hydrocarbons:
mesitylene, biphenyl, naphthalene, durene, phenanthrene, pentamethylbenzene,
hexamethylbenzene, pyrene, anthracene, 9,10-diphenylanthracene, benzo(a)pyrene,
and benzo(e)pyrene, was studied in the $AlCl_3$:BuPyCl systems in the 0.75:1 to
2:1 molar ratio, at $40^\circ C$.[56] All the hydrocarbons studied were shown to
undergo a one-electron oxidation to the radical-cation at a potential that
is independent of the melt composition. The radical-cations in these molten
salt systems were found to be more stable than in acetonitrile.[60-63]

Figure 3 illustrates a linear correlation between the half-peak
potential (proportional to the half-wave potential) and the first ionization
potential (IP) of the parent hydrocarbon determined from photoelectron
spectroscopy.[64-65] The equation:

$$E_{p/2} = 0.61 \; IP - 3.34 \tag{11}$$

was found to fit the experimental data with a correlation coefficient CC=0.97.
An analogous correlation with similar slope and intercept was obtained using
the data from acetonitrile experiments [60-63] (CC=0.96). These findings suggest
that there is no strong interaction between the acid species in the melt and
the hydrocarbons.

After referring all $E_{p/2}$ potentials to that of the ferrocene/ferricinium
ion couple in the melt and in acetonitrile, it has been observed that the
oxidation potentials in the melt are about 0.1 V positive to those in
acetonitrile, implying that it is slightly more difficult to oxidize these
compounds in the melt than in acetonitrile.

Though the electrochemical data and correlations with IP seem to

suggest that the hydrocarbons do not interact with acid species in the melt, it was observed that some of the hydrocarbon solutions change color in acid melts suggesting that the hydrocarbons interacts with the solvent. When these solutions are made basic by addition of BuPyCl, they can be reversibly decolorized.

There are several reports in the literature of the existence of solid state σ-complexes between $AlCl_3$ and hydrocarbons.[68-71] Table II compares the UV-visible spectra of solutions of some of the hydrocarbons studied in the 1.2:1.0 $AlCl_3$:BuPyCl melt and the solid state σ-complexes.[66-69] It has been found that in melts more basic than 1.0:1.0, the spectra obtained correspond to those of the parent hydrocarbons. Though extinction coefficients were not reported, it has been observed that as the acidity increases, the intensity of the colored species increased. This behavior indicates that an acid-base type equilibrium between acid species in the melt, $Al_2Cl_7^-$, and the hydrocarbons is occurring. It has been suggested than an equilibrium of the type:

$$\text{(anthracene)} + Al_2Cl_7^- \rightleftharpoons \text{(σ-complex)} + AlCl_4^- \qquad (12)$$
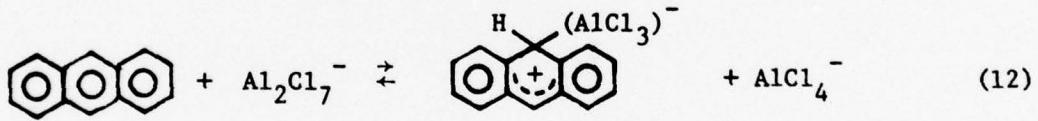
similar to that involved in the formation of carbonium ions[70] may exist, as in the example shown with anthracene. From the absence of any acid-base effects in the electrochemical oxidations of these hydrocarbons in the $AlCl_3$/BuPyCl melts it was concluded that either the equilibrium of Eq. 12 is very fast and the hydrocarbon is more readily oxidized than the σ-complex or alternatively the σ-complex and the hydrocarbon oxidize at the same potential.

An interesting but so far puzzling phenomenon was observed in acid melts for hydrocarbons with a $E_{p/2}$ of less than 1.4 V at a glassy carbon electrode vs. Al reference electrode. In the more acid melts, these hydrocarbons (hexamethylbenzene, pyrene, anthracene, 9,10-diphenylanthracene, benzo(a)pyrene and benzo(e)pyrene) are slowly but spontaneously oxidized to the cation radicals by the molten salt itself. The nature of the oxidizing agent or its reduction product is unknown. The spontaneous oxidation ceases when the acidity of the melt is lowered.

4d. Electrochemical Study of the Fe(III)/Fe(II) System

Hussey and King[57] have studied the Fe(III)/Fe(II) electrode reaction in the 2:1 $AlCl_3$:BuPyCl melt at $30^{\circ}C$ and in the 1:1 $AlCl_3$:BuPyCl melt at $35^{\circ}C$, employing a rotating disc electrode, cyclic voltammetry and potentiometry.

At a glassy carbon or tungsten working electrode in the acid melt the reduction $Fe(III) + e^- \rightarrow Fe(II)$ was found to be moderately rapid, with a standard heterogeneous electron transfer rate constant of 1.3×10^{-4} cms^{-1} and $\alpha = 0.4$. The heat of activation for this process is ~60 kJmol^{-1}. From Nernst plots the standard electrode potential (E^{o}) for the Fe(III)/Fe(II) couple at $30^{\circ}C$ is 2.01 V, with a $dE^{o}/dt = 9.5 \times 10^{-4}$ mV/$^{\circ}C$. From rotating disc data, the diffusion coefficient of the electroactive species was found to be 4.4×10^{-7} cm^{2}s^{-1}, with an activation energy for diffusion of 21 kJmol^{-1}.

The electrochemical reduction of Fe(III) in the basic melt is a one-electron reverisble process. The standard electrode potential is 0.125 V ($35^{\circ}C$) with $dE^{o}/dt = 4.7 \times 10^{-4}$ mV/$^{\circ}C$. The diffusion coefficient of the electroactive species in this medium is 4.6×10^{-7} cm^{2}s^{-1} ($35^{\circ}C$).

The marked increase in the rate of the Fe(III)/Fe(II) electrode reaction in going from the 2:1 to the 1:1 $AlCl_3$:BuPyCl melts, and also the almost 2 V difference in standard potentials coincides with the marked difference in anionic species observed in these melts, reported above. That the Fe(III) species present in these two media are different solvates and/or complexes is to be expected, and is further supported by the different colors exhibited by the ion in these media: orange (acid) to canary yellow (basic). A more complete conclusion about the nature of the species present in these media must await further investigations. The electrochemical behavior of Fe(III) ions illustrates the influence of the melt composition, therefore acidity, on the redox and coordination chemistry of this transition metal ion in these media.

5. CONCLUSIONS

The newly developed molten salt systems based on aluminum halides and alkylpyridinium halides, principally the $AlCl_3$:n-butylpyridinium chloride system, appear to be very suitable media for the study of chemical and electrochemical acid dependent reactions at a very convenient temperature range close to room temperature. It is worth emphasizing that these new ionic liquids offer new possibilities for structural studies over a wide range of temperatures. Miscibility of these molten salt systems with aromatic co-solvents such as benzene, toluene, etc., suggests the possibility of expanding the number of organic and organometallic compounds which may be investigated, in addition to improving the physical properties of the solvent system by decreasing the viscosity and increasing the electrical conductivity.

From a more practical point of view, it appears that these systems may also be useful battery electrolytes. Research of possible electrode systems is therefore another branch for future research.

6. ACKNOWLEDGEMENTS

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TABLE I

Summary of experimental Raman frequency shifts (cm^{-1}) for aluminum chloride:
1-butylpyridinium chloride mixtures at room temperatures
from reference 54.

Molar Ratio $[AlCl_3]:[RCl]$				
0.75:1.0	1.0:1.0	1.5:1.0	1.75:1.0	2.0:1.0
			−95 sh	−102 sh
−126 sh (0.9)	−127 sh (1.3)	−126 sh		
		−159 (1.2)	−163 (1.5)	−163 (2.3)
−186 (2.1)	−184 (2.0)	−183 (2.8)	−183 (1.6)	−182 (0.9)
−298 (0.9)	−295 (0.7)	−296 sh (1.4)	−295 sh (1.6)	−295 sh (1.1)
		−314 (8.8)	−316 (10.0)	−315 (10.0)
−351 (10.0)	−352 (10.0)	−351 (10.0)	−352 (5.0)	
−433 (0.1)	−433 (0.1)	−434 (2.7)	−433 (3.3)	−434 (2.2)
−485 (0.5)	−483 (0.4)			
−653 (2.8)	−650 (2.4)	−651 (3.2)	−647 (4.7)	−651 (2.7)
−775 (0.7)	−770 (0.5)	−774 (0.2)	−772 (0.2)	−769 (1.0)

TABLE II

Spectroscopic data for aromatic hydrocarbons in a 1.2:1 aluminum chloride:n-butylpyridinium chloride molten salt[56] and for solid state complexes with $AlCl_3$.[68,69,71]

Aromatic Hydrocarbon	λ_{max}/nm Melt[56]	λ_{max}/nm Solid State Complex
Mesitylene	367	365[69]
Durene	382	380[69]
Pentamethylbenzene	380	385[69]
Hexamethylbenzene	398	400[69]
Naphthalene	393	410,[69] 377[71]
Phenanthrene	417	425,[69] 653[71]
Pyrene	451, 465, 475, 492	520,[69] 480[71]
Anthracene	417	418,[71] 560,[69] 420[68]

TABLE III

Physical properties of some alkyl pyridinium halide – aluminum halide melts from reference 47.

Melt	Temp/$^{\circ}$C	Density/g.cm^{-3}	Viscosity c.p.	Electrochemical Window/V[a]
2:1 AlCl$_3$:BuPyCl	25	1.33	27.0	0.0 to 2.1
1:1 AlCl$_3$:BuPyCl	40	1.24	20.9	-0.4 to 2.0
2:1 AlCl$_3$:EtByPr	25	1.52	25.0	-0.2 to 1.8
2:1 AlBr$_3$:EtByPr	25	2.20	~50	0.2 to 1.6

a) At a glassy carbon electrode versus an Al wire reference electrode in the same melt.

Figure 1

Potentiometric data for $AlCl_3$:1-butylpyridinium chloride versus $Al(O)/2$:1 mole ratio mixture reference; x $30^{o}C$, O $60^{o}C$, ● $120^{o}C$; —— theory ($30^{o}C$). After Gale and Osteryoung.[55]

MOLE RATIO AlCl$_3$: BuPy Cl
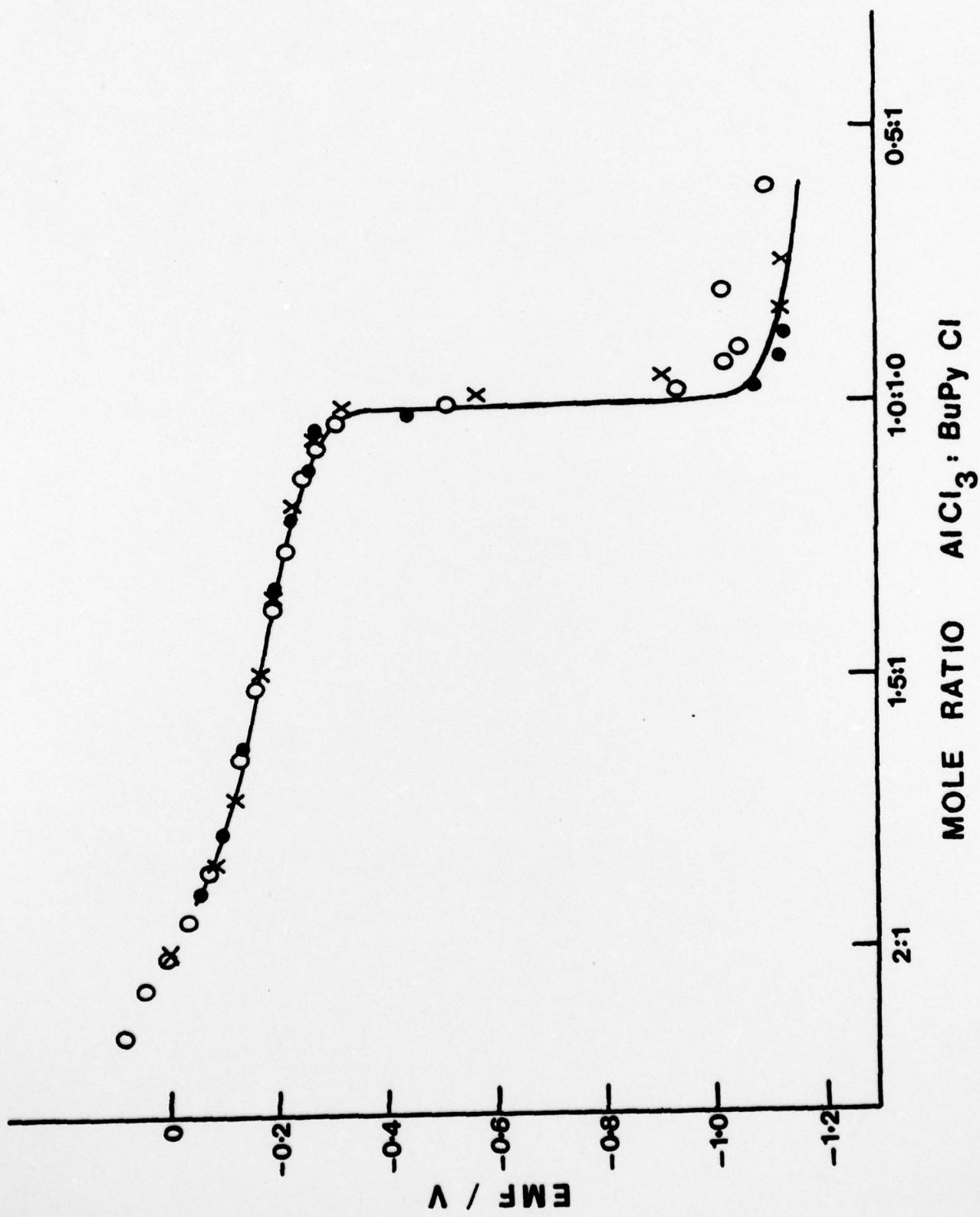
Figure 2

Mole fraction, N, of the major species in the melt at $30^{\circ}C$ as a function of the net $AlCl_3:RCl$ mole ratio. After Gale and Osteryoung.[55]

AlCl$_4^-$

Al$_2$Cl$_7^-$

Cl$^-$

MOLE RATIO

0·6:1 0·8:1 1:1 1·2:1 1·4:1 1·6:1 1·8:1

−2 −4 −6 −8 −10 −12 −14

LOG N
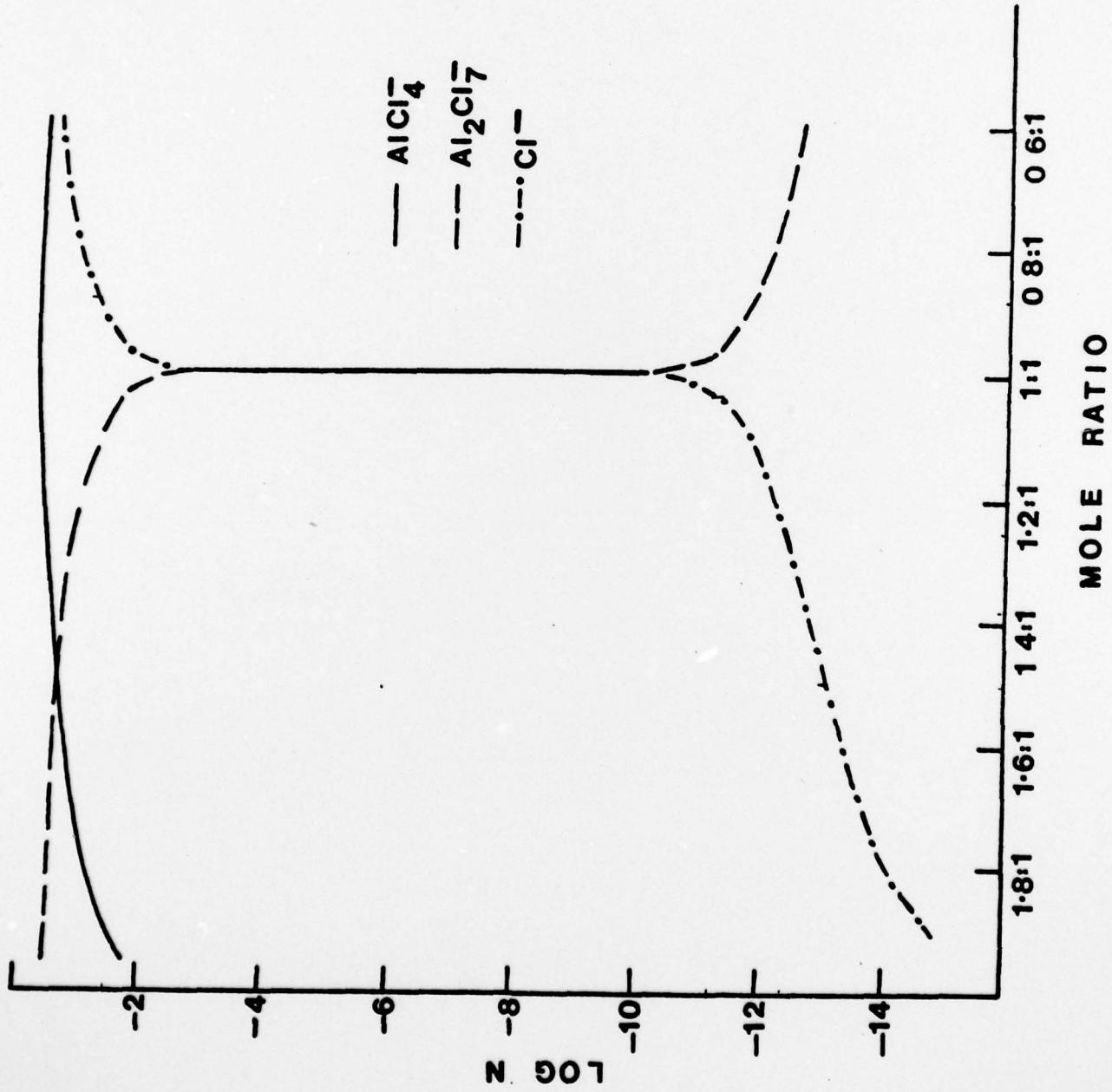
Figure 3

The correlation between $E_{p/2}$ values for the oxidation of aromatic hydrocarbons in the $AlCl_3$:n-butylpyridinium chloride molten salt and their photoionization potentials. (1) Mesitylene; (2) Biphenyl; (3) Napthalene; (4) Durene; (5) Phenanthrene; (6) Pentamethylbenzene; (7) Hexamethylbenzene; (8) Pyrene; (9) Anthracene; (10) 9,10-Diphenylanthracene; (11) Benzo(a)pyrene; and (12) Benzo(e)pyrene. After Robinson and Osteryoung.[56]
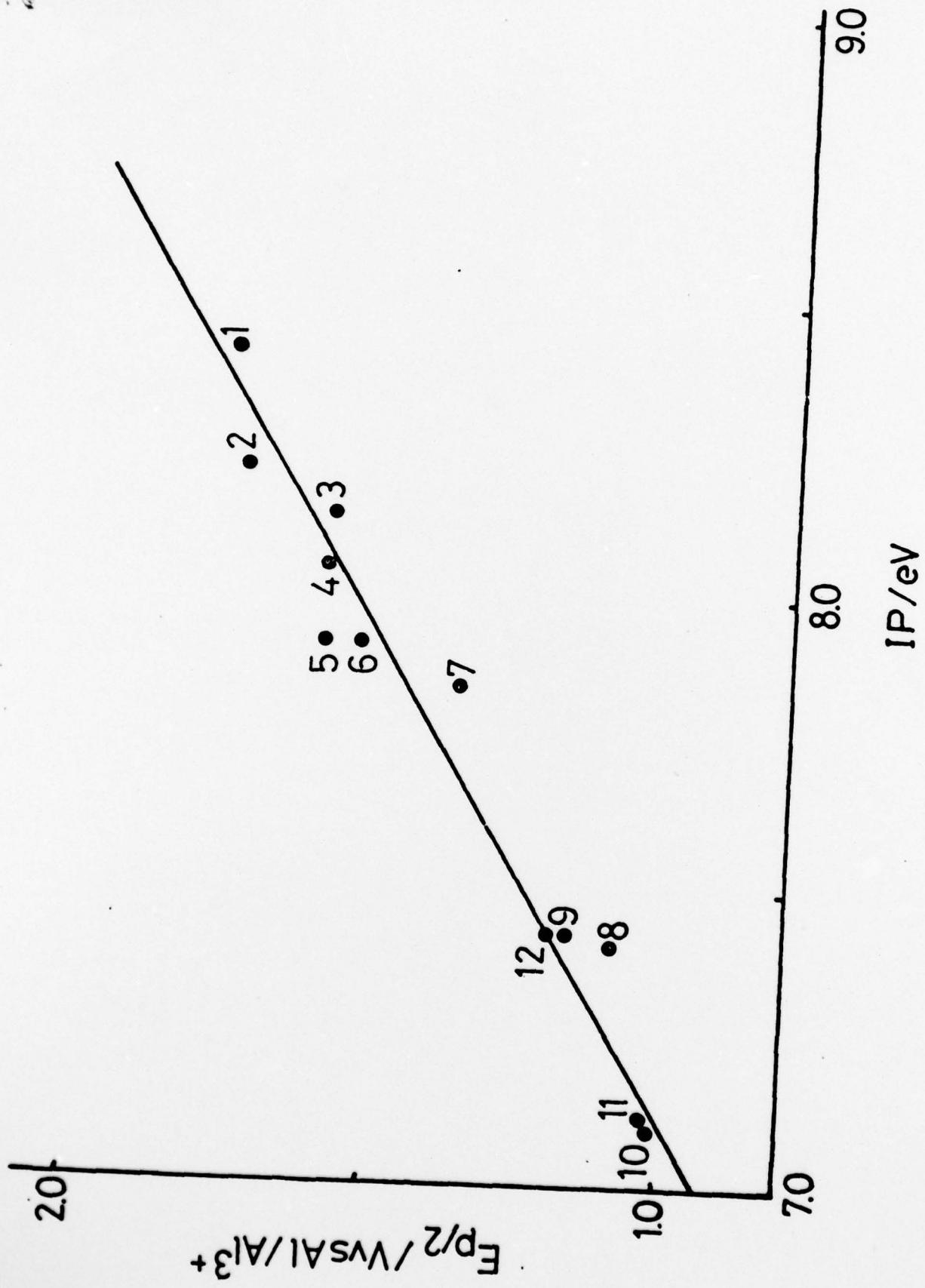
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